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W A LANFORD ET AL. 1982

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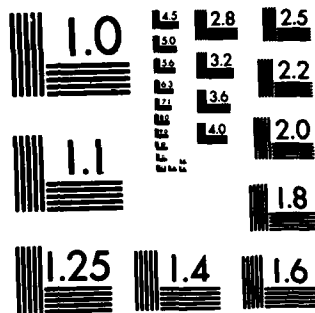
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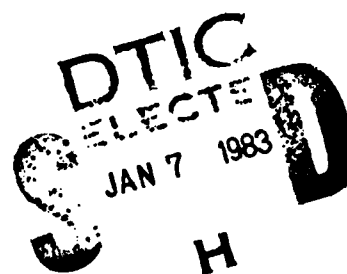
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SUNY/ALBANY GLASS STUDY GROUP

1981 - 82 ANNUAL REPORT

W. A. Lanford

C. Burman



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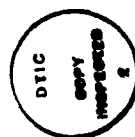
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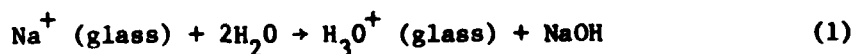


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I. Introduction

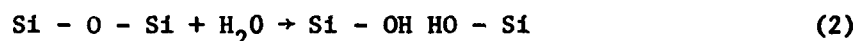
Glass is one of the most durable materials commonly made. Both the chemical durability and the fracture strength of glass are largely determined by chemical reactions occurring at the glass surface. Under most conditions, it is reactions between the glass and water or aqueous solutions that are the leading steps in surface degradation. While glass's desirable properties have made it a choice material for container and other "glass wares" for thousands of years, there is ever increasing interest in its chemical durability because of new technological uses such as in optical devices (communication networks, high energy lasers...) and as a consolidating medium for radioactive waste storage. Because of the absence of a long history of use for these newer applications, it is especially important to have a knowledge of the mechanisms responsible for the reaction between water and glass in order to design the glass and to make reliable predictions about the long term behavior of these materials when exposed to various environments.

The reaction between water and an alkali silicate glass proceeds through at least two distinct stages. The first is an ion exchange reaction of a hydrogen bearing cation from water with an alkali ion in the glass^(1,2). While there is still some uncertainty about the precise nature of the hydrogen bearing ion, most evidence indicates it is hydronium (H_3O^+) that is responsible for the transport of hydrogen into the glass⁽¹⁾. For a soda glass, this ion exchange reaction would be:



This reaction provides a flux of H_3O^+ ions which interdiffuse with Na^+ ions from the bulk of the glass. The clearest delineation of this mechanism is given in reference (1).

The second distinct stage in the reaction between water and glass is the dissolution of the (ion exchanged) glass at the water-glass interface. The mechanisms responsible for this dissolution and the conditions influencing dissolution rate are not well understood. The basic reaction is the attack of the bridging oxygen bonds by water via the reaction:



eventually leading to dissolution.

In addition to the initial ion-exchange and "final" dissolution steps, evidence is accumulating that there is a definable intermediate step which we have referred to as a transformed surface layer. Evidence for this transformed surface layer is reviewed in reference (3).

We plan to continue our studies of the ion-exchange and dissolution reactions and to try and define more clearly the nature of the transformed surface layer. Further, we will try to determine what parameters (glass composition, ions in solution, etc.) influence the formation of this transformed surface layer. Since it seems to be this intermediate step which changes the relatively impervious and protective ion exchanged surface layer into a porous, easily attacked material, understanding the nature of the transformation and the parameters controlling its rate can be used both to design more durable glass surfaces and to project the long-term stability of glasses already in use.

These studies will continue to rely heavily on our facilities for

nuclear reaction analysis (for hydrogen and oxygen) and Rutherford backscattering spectrometry (for other elements) to measure quantitatively concentration profiles of various elements present near glass surfaces. During the first two years of our present ONR support we have spent considerable effort refining these techniques for the study of glass surfaces and we now have excellent facilities for carrying out these measurements. Because these techniques are quantitative without reference to standards, and because they allow us to follow the transport of the elements active in the chemical reaction by looking directly at changes in the glass surface (as opposed to trying to infer what has happened to the glass from analysis of what went into solution), these techniques have proved very powerful in defining the mechanisms controlling the reaction between water and glass.

II. Ionic Exchange, Interdiffusion, Transport and Dissolution

Interdiffusion

We have already completed a number of studies of the ionic exchange process^(1,3,4), and others are presently underway. These experiments generally involved measurement of the elemental profiles (using nuclear reaction analysis or Rutherford backscattering spectrometry) of H, Na, Ca, Cs, Sr. . .near glass surfaces exposed to water (or aqueous solutions) for various lengths of time. These measurements led to the development of a diffusion model with a transformed surface layer in which ionic mobilities are much higher than in dry glass⁽³⁾. This model successfully describes not only our own data but also the diffusion potential and

resistivity data of Wikby as well as data from other related experiments. These results indicate that glasses should be categorized into those that form transformed surface layers and those that do not, with those that do not being much more durable with respect to both ion exchange and dissolution processes.

Electrolysis

If the transport of hydrogen into glasses and alkali out of glasses is in the form of ions, this process can be modified by applying an external electric field. The measurement of the ion currents, changes in resistance of the glass and the elemental profiles resulting from the application of the field can be used to measure ion mobilities and to test alternative theories for the interdiffusion process⁽⁵⁾.

Carrying out these electrolysis experiments quantitatively (i.e. measuring total charge flows and conduction paths reliably) is proving deceptively difficult, and we are not yet satisfied with all of our results. We have carried out a series of measurements in collaboration with F. Ernsberger at PPG where we are trying to confirm the generality with which hydronium (H_3O^+) is the ion which carries current and replaces Na^+ in a soda-lime glass⁽⁶⁾. In these experiments, a series of glasses have been electrolyzed under different anode conditions, and the resulting changes in the composition of the glass near the anode have been measured. The goal was to measure directly the number of H and O atoms (e.g. 3 H and one oxygen if H_3O^+ is the ion) needed to carry one electronic charge (+e) into the glass surface.

While making these measurements, we have discovered one can electric-

ally drive not only the Na ions in a soda-lime glass but also Ca ions. The Ca ions appear to move only if there are no more mobile ions (e.g. Na^+ , H_3O^+) present. These results may be of importance for the modification of the optical properties of glass (such as in making optical wave guides or lenses) because of the large changes in the index of refraction accompanying changes in bi-alkali ion concentration in glasses. These results are presently being prepared for publication.

Effects of Ions in Solution

One of the surprising results we have observed is that even in pH neutral solutions, ions in solution can have dramatic effects on the ion exchange and dissolution reactions. This is dramatically shown in our data on the dissolution rate of a commercial soda-lime glass in concentrated saline (250 gm NaCl/lit). vs pure distilled water. The etch rate under otherwise identical conditions is three orders of magnitude greater in saline than in water.

Further, we have begun to study the effects of these salt ions on the ion exchange process, and we find equally dramatic effects. The presence of the ions increases both the $\text{Na} \leftrightarrow \text{H}$ -ion exchange rate and the rate of preferential leaching of Ca from the silica network. Indeed, no preferential leaching of Ca from a commercial soda-lime glass has been observed when the contact - even for a very long time - is with distilled water, whereas rapid Ca leaching is observed when the contacting solution contains NaCl.

We need to carry out additional measurements to try and understand the mechanisms by which these salt ions enhance the attack of glass by

water. Further, we have to go back and repeat some dissolution studies, controlling the contacting solution very carefully. The results we have obtained to date suggest that dissolution rates in pure distilled water are much smaller than previously reported, suggesting that previous results were dominated by effects of ions going into solution from the glass. Ion beam analysis techniques allow us to measure extremely small dissolution rates, thus providing the tools necessary to sort this question out.

Radiation Damage Effects

We have begun to use ion implantation techniques to study glass surfaces. Initially, the implantations were noble gases implanted as reference markers with which to measure dissolutions at the glass surfaces. We have also carried out some preliminary measurements of ion beam mixing of thin layers of metals evaporated onto glass surfaces. These ion beam mixings were stimulated by ion implantation of noble gases. In the future we would like to modify the elemental composition of the near surface region of glasses by introducing "foreign ions" by ion implantation (or ion beam mixing) in order to study the effects of these foreign ions on ionic transport in the glass, structure and dissolution of glass surfaces.

If ion implantation is used to modify the elemental composition of a surface, the effects of the radiation damage which necessarily accompanies the ion implantation must also be studied. While the severity of the radiation damage effects depends on the implanted ion, its energy and, most importantly, on the nature of the implanted material, insulators tend to be very easily radiation damaged.

We have begun the study the effect of radiation damage on the reac-

tion between water and glass, starting with what seemed to be the simplest case, fused quartz. The effects are dramatic. Normally, very little happens when fused quartz is in contact with water. However, if this glass is radiation damaged by even very few ions before being exposed to water, water rapidly penetrates into the fused silica to high concentrated ions. While more measurements are needed, perhaps what is happening is that the bombarding ions create chemically very reactive defects (oxygen vacancies?) which react with the water.

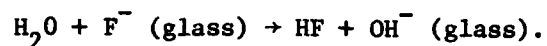
We also have begun to study these effects in the more complicated case of an alkali silicate glass where we find the damage influences both the ionic transport and dissolution mechanisms.

These radiation damage effects are intrinsically interesting and need to be studied. However, one of our prime interests is to use ion implantation to modify surface compositions. From this point of view, radiation damage is an unfortunate complication. Hence, our next step will be to explore various annealing procedures with the goal of removing the radiation damage without allowing the implanted ions to diffuse away. We hope that this goal can be reached with a conventional thermal annealing cycle. If a rapid cycle is needed, laser, electron or ion beam annealing are possible, but there appear to be problems associated with these methods which would restrict the range of their application.

Durability of Fluoride Glasses - Another Ion Exchange Mechanism?

A number of materials are fluoride ion conductors; these include both fluoride glasses as well as some crystalline materials such as PbF_2 . If such a material is exposed to the atmosphere and atmospheric water, one may expect an $\text{F}^- \leftrightarrow \text{OH}^-$ ion exchange reaction to occur followed by the

ionic interdiffusion of OH^- into the glass and F^- out. The reaction would be



In a post-deadline paper at the Cincinnati Meeting of the American Ceramic Society, Simmons et al (Catholic University) presented data on the reaction between water and fluoride glass. Their method was to analyze what went into solution. They found that the solution became more acidic as the reaction proceeded. We have measured hydrogen concentration vs depth for one fluoroide glass exposed to air, and we find a concentration profile consistent with ionic interdiffusion of F^- with OH^- with $D_{\text{OH}}/D_{\text{F}} = 10$.

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Journal of Material Science (in press).
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5. R. H. Doremus
Journal of Non-crystalline Solids (accepted).
6. See 1980-81 Annual Report pg. 17-24 and
W. A. Lanford, C. Burman and F. M. Ernsberger
Abstract, Fall Meeting of Glass Division of American Ceramic
Society, Bedford Springs, PA, September 29 - October 1, 1982.

II. Accomplishments

Publications

Work completed and prepared for publication from October 1980 - August 1981) is included in the following list of publications. In addition, descriptions of some research projects in progress but not yet published are contained in the 1980-81 Annual Report of the SUNY Glass Study Group.

A. Analysis with Heavy Ions

W. A. Lanford
In Heavy Ion Science, D. Allan Bromley editor
Plenum Press, New York (to be published).

B. Nuclear Reaction Analysis for Hydrogen

W. A. Lanford
Invited paper to appear in Proceeding, Symposium on
Advanced Techniques for the Characterization of Hydrogen
in Metals, The Metallurgical Society of AIME Meeting,
October 11-15, 1981, Louisville, Kentucky.

C. Nonequilibrium Water Permeation in SiO_2 Thin Films

R. Pfeffer, R. Lux, H. Berkowitz, W. A. Lanford and C. Burman
Journal of Applied Physics 53 (1982) 4226.

D. Measurement of Three Dimensional Distributions of Hydrogen in Thin Samples Using the ^{15}N Hydrogen Profiling Method

W. A. Lanford and C. Burman
Proceeding, International Symposium on the Electronic Structure
and Properties of Hydrogen in Metals, March 4-6, 1982,
to be published.

E. Application of Ion Beam Techniques to the Study of Glass Durability: Enhanced Dissolution in Saline and Radiation Effects

C. Burman, Wang Ke-Ming and W. A. Lanford
Scientific Basis for Nuclear Waste Management, S. V. Topp, editor,
North Holland, New York (1982) 641.

F. Hydrogen Content of a Variety of Plasma-Deposited Silicon Nitrides

R. Chow, W. A. Lanford, Wang Ke-Ming and R. Rosler
Journal of Applied Physics 53 (1982) 5630.

G. A Technique for the Quantitative Measurement of the Three Dimensional Distribution of Hydrogen in Solids

W. A. Lanford and C. Burman
Applied Physics Letters 41 (1982) 473.

H. Reaction of Water with Glass: Influence of a Transformed Surface Layer

R. H. Doremus, Y. Mehrotra, W. A. Lanford and C. Burman
Journal of Material Science (submitted).

I. Hydration of Soda-Lime Silicate Glass: Effect of Alumina

T. A. Wassick, R. H. Doremus, W. A. Lanford and C. Burman
Journal of Non-Crystalline Solids (accepted).

J. Radiation Damage Enhancement of the Penetration of Water into Silica Glass

C. Burman and W. A. Lanford
Journal of Applied Physics (submitted).

K. Effects of Salt Ions on the Reaction Between Water and Glass

C. Burman and W. A. Lanford
Journal of American Ceramic Society (submitted).

L. Nuclear Reaction Analysis of Glass Surfaces: The Study of the Reaction Between Water and Glass

W. A. Lanford, C. Burman, R. H. Doremus, Y. Mehrotra and T. Wassick
To be presented at the Conference on Advances in Materials Characterization, University Series on Ceramic Science, August 15-18, 1982, Alfred, to be published in Proceedings.

M. Influence of Ion Implantation on the Reaction Between Water and Glass

C. Burman and W. A. Lanford
International Conference on Ion Beam Modification of Materials, September 6-10, 1982, Grenoble, France, Nuclear Instruments and Methods (accepted).

Because these papers are available, we will not report here a full description of these research efforts. Instead, we will provide a very brief outline of where the research reported in these papers fits within the overall goal of our research. Abstracts of these papers are attached to this report.

Development of Ion Beam Analysis of Glass Surfaces

The goal of our research effort was to further our knowledge of the mechanisms responsible for the reaction between water and glass. We planned to do this making special use of nuclear reaction analysis (especially for hydrogen analysis) and Rutherford backscattering to measure changes in the elemental composition near glass surfaces as a result of reactions with water. Hence one of our first goals was to put in place at SUNY/Albany the necessary analysis chambers, etc., to carry out these analyses and to refine these techniques to take account of the special problems associated with ion beam analysis of glass. The general principles and application of these techniques are reviewed in two papers (A, B). Paper E discusses the combination of ion implantation and ion beam analysis to study interdiffusion and dissolution and briefly describes some of our very surprising results as to the effect of salt in solution and radiation damage on the reaction between water and glass.

One of the important accomplishments in the development of these ion beam analysis techniques was not anticipated. During the preparation of paper B, we realized that we could develop a technique for measuring full three dimensional distributions of H in solids by forming autoradiographs of the lateral distribution of H. This new method is described in papers D and G and is potentially of great importance in the study of stress-corrosion induced fracture in metals and ceramics.

In paper L we describe carefully the application of high energy ion beam analysis to the study of glass surfaces with emphasis on the unique capabilities of these techniques.

Study of Transport into Glass Surfaces

One of our main research efforts was to use ion beam analysis to measure the concentration profiles of the constituents of glass as a function of hydration time. Papers H and I describe some of these results, and more measurements are in progress. These data confirm that the ionic exchange and interdiffusion are the first steps in the reaction between water and all these glasses, but that this ion exchanged surface layer can undergo a structural transformation. This model is described in paper H, where both our data and the results of others are considered.

The next natural progression in this research is to try to refine our understanding of this transformed surface layer and determine what parameters govern its formation.

We have also started measurements of where ions have been driven into the glass surface by an applied electric field. These electro-migration experiments show that Na and H ions can be driven electrically, as expected. In addition, if there are no more mobile charge carriers available, Ca ions will also migrate in an applied field. These experiments are being carried out in collaboration with F. Ernsberger and will be presented at the 1982 Fall Meeting of the Glass Division of the American Ceramic Society.

We have also begun to study the diffusion of water into SiO_2 . To date, only measurements are for SiO_2 thin films grown on silicon and are published (paper C). We also have data at low temperatures ($<100^\circ\text{C}$) for water diffusing into fused quartz. These experiments are difficult because

of the very low levels of hydrogen (~ 1 ppt atomic) even in saturated films. Measurement of these profiles required significant improvement in the sensitivity of our ^{15}N hydrogen profiling procedure.

Effects of Ions in Solution on the Reaction Between Water and Glass

One of the unanticipated results of our application of ion beam techniques is that ions in solution, even in pH neutral solutions, have a dramatic effect on the reaction between water and glass. These results are discussed in papers E and K. Concentrated solutions of NaCl increase the etch rates of commercial soda-lime and borosilicate glasses by at least three orders of magnitude over the rates in distilled water. In soda-lime glass, the ions also greatly increase the preferential leaching of Ca and Na from the glass surface.

Radiation Effects

Because of our use of ion implantation to introduce reference markers for dissolution studies and because of our desire to modify surface compositions of glasses by ion implantation, we need to study the effects of the radiation damage which necessarily accompanies this implantation. Even in the simplest silicate glass, fused quartz, the effects are dramatic. Ion implantation of even very few ions dramatically increase the penetration of water into this glass. This effect is described briefly in paper E and in detail in paper J.

We have also begun experiments with a commercial soda-lime glass, and these results are reported in paper M.

Etching of Amorphous Silicon Nitride

Paper F reports on the hydrogen content of amorphous plasma deposited silicon nitride made in a wide variety of reactor designs. The interesting observation is a correlation between dissolution rate and hydrogen content with etch rates varying over 3 orders of magnitude.

IV. Technological Significance

The discussion above is intended to give a general overview of our research results within the context of basic glass science and the question of the reaction between water and glass. However, because the reaction between water and glass has so many important technological consequences, we also wish to comment on the technological significance of some of our findings.

Fundamental Mechanisms

Most important is the realization that only if we develop an understanding of fundamental mechanism, can we hope to reliably predict effects. Glass (even when considering common silicate glasses) is a very varied material. If we can understand the fundamental mechanisms for transport in glasses and for the attack of the Si-O-Si network, we have the hope of predicting behavior over the full spectrum of glasses from remarkably durable SiO_2 to soluble simple two component glasses.

Optical Fibers and Optical Devices

Controlling OH

First, nuclear reaction analysis provides a unique method for determining the kinetics of the transport of water (or OH groups) into glasses. For many communication applications control of contaminant water was a crucial ingredient in making low loss fibers. To date, most of the work on reducing OH concentrations has been empirical. The optimization of procedures for reducing OH requires a better knowledge of the sources and transport modes of water in both the glass used to make the fiber and in its cladding. A number of our studies are relevant to this question.

For example, paper C presents a study of the kinetics of the penetration of water into SiO_2 thin films. We also have data on fused quartz at lower temperature (90°C) (unpublished). In the future it may be important to check that the results obtained for large planar bulk glasses can be safely applied to optical fiber geometrics. The autoradiograph technique for measuring lateral profiles of hydrogen (papers D and G) may make such measurements possible.

Second, the remarkable increase in the saturation level of water in SiO_2 as a result of radiation damage may be important (paper J and E). Clearly if SiO_2 optical devices are exposed to defect creating radiation, the rate with which they take up ambient water would be dramatically increased.

Third, the use of nuclear reactions to analyze for hydrogen has demonstrated that even technologically "clean" surfaces have large surface contaminations of hydrogen, typically 10^{16} H/cm^2 . This contamination persists unless extreme measures ($P \sim 10^{-10}$ Torr and special cleaning) are taken. At present, it is known how to make optical fibers with OH concentrations of less than parts per billion. At these very low levels, typical surface concentrations become a potentially important source of bulk OH.

Fracture and Fatigue

Perhaps the most obvious applications of our results are in the area of crack growth and fracture in glasses. While the basic ideas of Hillig and Charles that stress accelerated chemical reactions of water with glass leads to a sharpening of the crack tip are generally accepted, we need a

better understanding of these chemical reactions to apply these basic principles. We need to know both how the near surface glass is modified by reaction with water and how rapidly the glass near the crack tip is dissolving. The remarkable sensitivity of the dissolution rate of common glasses to ions in solution (pH neutral solutions) reported in paper K may cause some reanalysis of crack tip chemistry. Further, the study of how surface reactions (ion exchange, diffusion and dissolution) are influenced by stress would be an important contribution to the study of crack propagation. Unfortunately, it is difficult to maintain significant stress on glasses exposed to water or aqueous solutions. Further attempts at such stress experiments should be made.

In the future, it may be possible to use nuclear reaction analysis to measure the actual hydrogen distribution around a propagating crack. This measurement may be possible making use of the radiographic method described in papers D and G, or using microbeam techniques (presently under development). Such in situ measurements would fill in important gaps in data concerning slow crack growth. While such experiments are likely to be difficult, these nuclear reaction techniques for H analysis are the only ones known which seem capable of even attempting measurement of such H distributions.

Finally, we have the feeling that there may be a connection between the dramatic increase in the reaction between water and SiO_2 as a result of radiation induced defects (papers J and E) and in the increased reaction rate at the high stress region of a propagating crack. On a microscopic level, the crack tip can be considered as an extended defect.

Perhaps if we understand the chemistry of the radiation induced defects, we may gain some insight into the chemistry at propagating crack tip.

Long Term Durability of Rad-Waste Glasses

Much of our research has direct implications for the design and evaluation of glasses proposed to consolidate radioactive wastes. First, our furthering of the understanding of the ion exchange and dissolution reactions which occur whenever an alkali glass is exposed to water, is important when trying to analyze what happens for the very complicated rad-waste glasses. Second, the development of nuclear reaction analysis for H and backscattering for other elements to characterize changes in surface composition (both leaching and etching) has obvious application to the characterization of the weathering rates of rad-waste glasses. Indeed, these techniques are already being adopted in that community. Third, the dramatic increase in etch rate of common soda-lime glasses in saline solution with increased concentration (paper K) was unanticipated and may be important to consideration of rad-waste glass long term storage environments. Finally, the study of radiation effects on the chemical durability of glasses is also of interest to the rad-waste glass problem.

V. Abstracts of Publications

ANALYSIS WITH HEAVY IONS

W.A. Lanford

Book chapter for Heavy Ion Science, D.A. Bromley, editor, Plenum Press

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NUCLEAR REACTION ANALYSIS FOR HYDROGEN*

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Albany, New York 12222

The use of resonant nuclear reactions to quantitatively measure hydrogen concentration vs depths in solids is described. The various reactions and experimental procedures used and the capabilities of these methods of hydrogen analysis are discussed. Application of these methods to a wide variety of fields is mentioned.

Invited paper presented at Symposium of Advanced Techniques for the Characterization of Hydrogen in Metals, The Metallurgical Society of AIME Meeting, October 11-15, 1981, Louisville, Kentucky.

* Research supported in part by a grant from the Office of Naval Research

⁺ An Alfred P. Sloan Foundation Fellow.

Nonequilibrium water permeation in SiO₂ thin films

Robert Pfeffer, Robert Lux, and Harry Berkowitz
U. S. Army Electronics Technology and Devices Laboratory (ERADCOM), Fort Monmouth, New Jersey 07703

W. A. Lanford and C. Burman
Department of Physics, State University of New York, Albany, New York 12222

(Received 6 January 1982; accepted for publication 21 February 1982)

Nuclear resonance profiling was used to measure the distributions of hydrogen incorporated into dry SiO₂ films by thermal treatments in steam. Thermal oxides were grown on silicon to a thickness of 260 nm in dry O₂ and were subsequently treated in steam at temperatures of 320 and 500°C for periods lasting between 390 and 6 × 10³ s. The concentrations of hydrogen carried in by permeating water were then profiled with 6.4 MeV ¹⁵N ions using the resonant nuclear reaction ¹H(¹⁵N, αγ)¹²C. Water was seen to penetrate the films rapidly and to slowly react with the SiO₂ uniformly throughout the films. Two distinct stages were observed in the buildup of H, indicating that the water/SiO₂ reaction involves at least two concurrent processes rather than a single-stage process.

PACS numbers: 66.30. - h, 68.60. + q, 81.60.Dq

Thermal oxidation of silicon to form high-quality insulating films of SiO₂ is an important process in modern electronic technology. The properties of the oxides formed by this process have been found to depend critically on the presence of water absorbed in the films either during oxidation or in subsequent high temperature processing. An example of this is the recent observation¹ of morphological differences between wet and dry ultra-thin metal-oxide-semiconductor (MOS) gate oxides: wet films were seen to be free of the micropores present in dry films and showed better breakdown resistance. Physical models of the diffusion and incorporation of water in SiO₂ have received comparatively little experimental testing. In an early study of water diffusion in fused silica, Moulson and Roberts² proposed that the transport involved mobile OH groups arising from the reaction



at the outer surface. They modeled the process with Fick's second equation using a constant effective diffusion coefficient

$$\partial [\text{OH}]/\partial t = D_{\text{eff}} \nabla^2 [\text{OH}], \quad (2)$$

determining D_{eff} by observing the time behavior of the total OH content during the early stages of steam absorption and vacuum desorption. An alternative model, proposed by Doremus,³ was the transport of dissolved molecular water through "doorways" between cells or interstices in the network, with the SiOH groups produced by reaction (1) being immobile. He also assumed (a) that the reaction proceeded rapidly compared to diffusion, allowing the equilibrium concentrations of diffusing water and SiOH groups to be related by the law of detailed balance

$$[\text{H}_2\text{O}] = [\text{OH}]^2/K^2, \quad (3)$$

and (b) that the water concentration and its time derivative were negligible compared to those for SiOH. These assumptions led him to model the process with the concentration-dependent diffusion equation

$$\partial [\text{OH}]/\partial t = (2D/K^2) \nabla^2 [\text{OH}]^2, \quad (4)$$

where D and D_{eff} are related by $D_{\text{eff}} = 2D [\text{H}_2\text{O}]/[\text{OH}]$. This produced a much better match to the [OH] profiles measured by Roberts and Roberts⁴ in fused silica than is possible with a solution to Eq. (2). (A profile measured by Moulson and Roberts was insufficiently precise to distinguish the two models.) This model, unlike the earlier one, also implies a larger effective diffusivity for absorption than for desorption, consistent with the measurements of Moulson and Roberts. Doremus also used this model to treat the steady-state steam oxidation of silicon,⁵ relating the temperature and pressure dependence of the parabolic oxidation-rate constant to that of D_{eff} .

Doremus' model applies to the regime where equilibrium has been established between [H₂O] and [OH]. Our previous observations⁶ of tracer ¹⁸O exchange during water diffusion at relatively low temperatures were generally consistent with this model. However, we saw evidence of a systematic trend toward anomalously low exchange rates during the early stages of absorption in dry oxides. This suggested that the [OH] had not reached its saturation value, contrary to our expectation from Eq. (4) that it should have reached it on a time scale of x_0^2/D_{eff} , where x_0 is the film thickness. We therefore decided to investigate the early behavior of water absorption in dry oxides.

Samples were prepared by forming thermal oxide films in nominally dry O₂ at 1100°C on (100) surfaces of 5 Ω cm (nominal) *n*-type silicon to a thickness of 260 nm. The samples were subsequently treated in flowing steam at 1 atm according to the procedure described in Ref. 6. Formation of additional oxide during the steam treatments was negligible. The concentrations of hydrogen carried in by absorbed water were then profiled with 6.4 MeV ¹⁵N⁺⁺ ions⁷ by detecting the characteristic 4.4-MeV gamma rays from the resonant nuclear reaction ¹H(¹⁵N, αγ)¹²C. The beam current was about 40 nA and the beam spot was about 3 × 10 mm, producing negligible sample heating. Data collection lasted about 8 min at each beam energy. The integrated ion-beam current was 24 μC at each beam energy.

Detailed profiles of the near-surface regions showed

Paper presented at "International Symposium on The Electronic Structure and Properties of Hydrogen in Metals", March 4-6, 1982, Richmond, Virginia.

To be published in the proceedings, Editor P. Jena.

MEASUREMENT OF THREE DIMENSIONAL DISTRIBUTIONS OF HYDROGEN IN THIN SAMPLES USING THE ^{15}N HYDROGEN PROFILING METHOD

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ABSTRACT

The use of the $^{15}\text{N}+^1\text{H}+^{12}\text{C}+^4\text{He}+\gamma$ -ray resonant nuclear reaction, with ^4He particles recorded in plastic track detectors, is described as a method of measuring full three dimensional distributions of H in thin samples. To use this reaction to measure H concentrations, the sample is bombarded with ^{15}N ions at an energy greater than the resonance energy at which the reaction occurs. As these ions penetrate the sample, they lose energy and reach the resonance energy at some depth. The yield of ^4He particles from the reaction is proportional to the concentration of hydrogen at that depth. By recording the He particles in plastic track detectors, an autoradiograph of the lateral hydrogen distribution at the resonance depth is obtained. Limitations and potentials of this method are discussed along with some measurements of distributions of H ion implanted into silicon.

INTRODUCTION

Analysis for hydrogen is notoriously difficult. It's atomic charge is too small for Auger or x-ray methods, and it is mobile and so common a contaminant in vacuum systems that many ion beam techniques are unsatisfactory. The one quantitative technique which has become widely used over the past five years is nuclear reaction analysis (NRA).

⁺An Alfred P. Sloan Foundation Fellow

APPLICATION OF ION BEAM TECHNIQUES TO THE STUDY OF GLASS DURABILITY:
ION-BEAM IMPLANTATION IN SALINE AND RADIATION EFFECTS*

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ABSTRACT

Nuclear reaction analysis, Rutherford backscattering and ion implantation techniques are applied to the study of the reaction between glass and aqueous solutions. The use of these techniques is described as are some of the results obtained. Solutions of NaCl are seen to etch some glasses several orders of magnitude faster than distilled water. Radiation damage created by high energy heavy ion bombardment is seen to have great effects on the penetration of hydrogen (water) into glass.

INTRODUCTION

Glass is one of the most durable materials commonly made. Indeed, it is because of its durability and ease of manufacture that glass has been commonly used to make containers for both commercial and scientific wares for thousands of years. The relatively recent need to develop materials to consolidate and isolate radioactive wastes for long periods of time presents new challenges both for more durable materials and for new procedures for characterizing durability. Central to the question of glass durability is the reaction between water (or aqueous solutions) and glass. The present paper describes the application of ion beam analysis techniques to the study of the reactions between water and glass and presents some of our results.

While it is glass's durability that makes it an interesting material, it is this same property that makes it difficult to study the chemical reaction between water and glass. Traditional analytical methods become difficult to apply when the amount of reaction product becomes too small. While a number of clever techniques have been developed to obviate these difficulties, generally these methods rely on rather indirect evidence to try to deduce what is happening at the glass-water interface. However, by applying ion beam analysis techniques, such as Rutherford backscattering spectrometry and nuclear reaction analysis, one can measure the concentration vs depth of the active elements (such as H, Na, K, Ca, Cs, etc) at and near the surfaces of glasses which have been exposed to water. These techniques not only are quantitative but also have good sensitivity and depth resolution, and, hence, can provide key information useful to help understand the mechanisms which govern this chemical reaction.

In addition, by using ion implantation to imbed a "marker" into a glass sample which is subsequently exposed to an aqueous solution, one can measure the dissolution (etch) rate of glasses with great sensitivity.

* Research supported in part by the Office of Naval Research (R. Pohanka).

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Hydrogen content of a variety of plasma-deposited silicon nitrides

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(Received 12 February 1982; accepted for publication 20 April 1982)

The hydrogen contents and etch rates have been measured for plasma-deposited silicon nitrides made in nine different commercially available reactors as well as for some low pressure chemical vapor deposited nitrides. The hydrogen contents vary from 4% to 39% (atomic). A correlation is observed between etch rate and hydrogen content, with etch rates varying over three orders of magnitude.

PACS numbers: 61.70.Wp

I. INTRODUCTION

"Silicon nitride" made by a variety of plasma-enhanced deposition processes is gaining increased use in the fabrication of microelectronic devices. While it is widely recognized that the materials referred to as plasma-deposited silicon nitride do not have a fixed stoichiometry but rather contain varying amounts of Si, N, and H, investigations of effects of various deposition conditions on stoichiometry have been few. The paucity of studies results not from lack of interest but rather from the difficulty of making quantitative analysis of the composition, especially the hydrogen content, of these thin film materials. Hydrogen is invisible to most of the traditional analytic methods, such as Auger spectroscopy or Rutherford backscattering spectrometry, commonly used to study thin film materials.

Nuclear reaction analysis—the one quantitative method available for measuring the hydrogen content of thin films—has been applied in a few cases^{1,2} with the general result that these materials contain large amounts of hydrogen, typically 10–35% (atomic). That is, in spite of the generic name *silicon nitride*, these materials contain essentially as many H atoms as silicon or nitrogen atoms.

In previous studies of this material^{1–6} researchers have concentrated on studying the systematics of nitrides made in a single reactor by varying deposition conditions (e.g., gas pressures, flow rates, impurities, and substrate temperature). It is difficult to draw universal conclusions valid for all plasma-deposited silicon nitrides from such studies because of different (and often difficult to monitor) deposition conditions in different reactor designs. The present study attempts to avoid this difficulty by studying films made both by varying reactor design and by varying deposition conditions for a single design. Also included in this study are data from two samples of low pressure chemical vapor deposition (LPCVD) silicon nitride.

From the study of the hydrogen content of materials made by most of the commercially available reactors we ob-

serve a seemingly universal relationship between hydrogen content and buffered oxide etch (BOE) rate.

II. EXPERIMENTAL PROCEDURE

A. Film deposition

In one part of this study, silicon nitride films were prepared in nine different reactors using the standard recommended processing parameters. These reactors, identified by the commercial vendors, are tabulated in Table I. In most cases, two samples from each reactor were independently studied. In addition two samples were also prepared using

TABLE I. H content and etch rate.

| Sample | H content At % | Etch rate Å/min |
|---|----------------|-----------------|
| AMT 23 ^a | 22.4 | 200 |
| AMT 24 ^a | 21.2 | 190 |
| ASM 29 ^b | 19.2 | 55 |
| ASM 30 ^b | 19.2 | 60 |
| Commonwealth Scient. 37 ^c | 26.2 | 440 |
| Commonwealth Scient. 38 ^c | 26.9 | 523 |
| Ionic System 59 ^d | 29.0 | 740 |
| Ionic System 62 ^d | 26.9 | 696 |
| ET System 9 ^e | 22.4 | 120 |
| LFE 4 ^f | 15.4 | 85 |
| LFE 3 ^f | 15.4 | 61 |
| PWS 27 ^g | 17.4 | 40 |
| PWS 0 ^g | 19.4 | 45 |
| Plasma Therm 25 ^h | 24.9 | 580 |
| Plasma Therm 26 ^h | 24.5 | 560 |
| Tegal 15 ⁱ | 30.6 | 1220 |
| Tegal 16 ⁱ | 30.7 | 1240 |
| Si ₃ N ₄ B ^j | 4.1 | 6 |
| Si ₃ N ₄ F ^j | 4.6 | 12 |

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Technique for the quantitative measurement of the three-dimensional distribution of hydrogen in solids

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(Received 26 May 1982; accepted for publication 11 June 1982)

A technique for measuring full three-dimensional concentration profiles of hydrogen in solids is proposed and demonstrated. The technique uses the resonant nuclear reaction $^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + \text{gamma ray}$ to probe for hydrogen in thin samples with the ^4He particles emitted in forward directions used to form an autoradiograph of the lateral distribution of hydrogen within the sample. Results from a demonstration example of H implanted through a mask into silicon are reported.

PACS numbers: 61.70.Wp

Most modern analytical methods do not work for hydrogen because of its low Z and low mass. Because of this lack of suitable analytic methods, because of the observation that hydrogen appears to be a nearly universal contaminant and because even small amounts of hydrogen can have dramatic effects on the properties of many materials, techniques for the quantitative analysis for hydrogen based on nuclear reactions have been developed and are now widely used.¹⁻⁴ These techniques have been very successful in determining the concentration versus depth of hydrogen but have not been able to measure the lateral distributions of hydrogen. While most ion beam analysis techniques have been extended to measure lateral distributions by focusing the incident ion beam to a microbeam (typically of order 1–10 μm) and rastering this beam across the sample, such microbeam techniques appear not to work reliably for hydrogen because of hydrogen's high mobility in most materials. The high-energy density in a microbeam can be expected to drive the hydrogen away from the analyzing beam.

An alternative approach, first demonstrated for deuterium analysis by Ilıc and Altstetter,⁵ is to bombard with a large uniform ion beam and use the radiations from nuclear reactions to form a prompt autoradiograph of the lateral distribution of deuterium within their sample. In many problems, it is essential to analyze for ^1H and not D because of the common presence of ^1H as a contaminant. Also, the relatively poor depth resolution of reaction used by Ilıc and Altstetter makes the discrimination between bulk and surface D difficult in many cases.

Because of the wide range of potential applications for a method which is capable of measuring both the lateral and depth distribution of ^1H in solids, we searched for possible nuclear reactions which could be used. The requirements were a narrow isolated resonance (for good depth resolution) with a large peak cross section (for high sensitivity) yielding an energetic ^4He particle which would have sufficient range that the incident ion beam could be ranged out, allowing the ^4He particles to be detected in a low background.¹ The nuclear reaction $^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + 4.4 \text{ MeV gamma ray}$, which is widely accepted as the most generally useful reaction for measuring depth profiles of hydrogen,² also seems particularly well suited for measuring lateral H pro-

files using autoradiographic techniques. Many potential nuclear reactions cannot be used because of the requirement that the emitted ^4He must have a significantly greater range than the range of the incident ion beam.

The present procedure is an extension of the well established ^{15}N hydrogen profiling technique.² In its usual application, the ^{15}N hydrogen profiling technique makes use of the narrow isolated resonance in the nuclear reaction: $^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + 4.4 \text{ MeV gamma ray}$ to measure hydrogen concentration versus depth. To use this reaction as a probe for hydrogen, the sample to be analyzed is bombarded with ^{15}N ions with an energy (E) equal to or greater than the resonance energy (E_r) at which the nuclear reaction can occur, and the yield of characteristic 4.4 MeV gamma rays is measured. By measuring the yield of characteristic gamma rays versus ^{15}N beam energy, the concentration of hydrogen versus depth is quantitatively determined.

The extension of this procedure makes use of the ^4He particles emitted in the nuclear reaction to determine the lateral distribution of the hydrogen within the plane parallel to the surface of the sample at the depth where $E = E_r$. This procedure is shown schematically in Fig. 1.

As indicated in Fig. 1, the sample is bombarded with ^{15}N ions with $E > E_r$. The sample must be in the form of a "thin section" with a thickness $\leq 10\text{--}20 \mu\text{m}$. At the depth where $E = E_r$, if there is hydrogen present, nuclear reactions

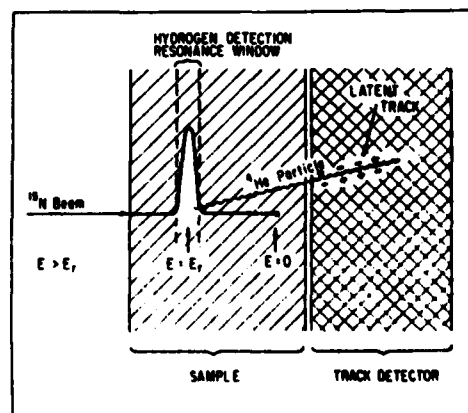


FIG. 1. Schematic representation of the autoradiographic technique for measuring lateral distributions of H in thin samples.

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REACTION OF WATER WITH GLASS: INFLUENCE OF A
TRANSFORMED SURFACE LAYER

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Abstract

Profiles of hydrogen and glass constituents were measured by nuclear reaction techniques in a number of silicate glasses after hydration. The results were interpreted in terms of interdiffusion of alkali and hydronium ions, including the possibility of a transformed surface layer. Durable glasses such as a commercial soda-lime and resium-alkali-lime glasses did not have a transformed layer, whereas less durable glasses, such as a soda-lime without alumina and a sodium-potassium-lime, did have a transformed surface layer. When a transformed layer is incorporated in the interdiffusion model, the diffusion coefficient of sodium calculated is the same as found in the dry glass.

HYDRATION OF SODA-LIME SILICATE GLASS
EFFECT OF ALUMINA

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ABSTRACT

Profiles of the elements in the surfaces of hydrated soda-lime silicate and soda-lime aluminosilicate glasses were measured with a resonant nuclear reaction (hydrogen) and Rutherford backscattering. The profiles were consistent with interdiffusion of sodium and hydrogen-bearing ions. Interdiffusion in the glass without alumina was faster, presumably because it had a transformed surface layer. A small amount of preferential leaching of calcium was detected in this glass.

Radiation Damage Enhancement of the
Penetration of Water Into Silica Glass^{a)}

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Abstract:

A dramatic increase in the rate of penetration of water into silica glass as a result of ion implantation with noble gas ions is reported. The damage caused by the implantation leads to the rapid uptake of water to a saturation concentration of hydrogen of approximately 10^{22} atoms/cm³. The effects of ion implant dose and ion mass are investigated. The results indicate that the mechanism responsible for this enhanced penetration is the creation of chemically reactive defects which greatly enhance the reaction between the water and the silica network.

Effects of Salt Ions in Solution on the Reaction Between Water
and Glass⁺

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Abstract

The effect of salt ions in solution on the reaction between water and a commercial soda-lime glass is investigated. It is seen that under otherwise identical conditions, glass etches orders of magnitude faster in saline than in pure distilled water. Ca is also seen to be preferentially leached when exposed to saline but not when exposed to distilled water. Glass radiation damaged by ion implantation of noble gases etches somewhat faster in saline than unimplanted glass.

⁺Research supported by the Office of Naval Research (R. Pohanka).

^{*}An Alfred P. Sloan Foundation Fellow.

Paper presented at the "Advances in Materials Characterization" Conference, August 15-18, 1982, Alfred University, Alfred, New York.

To be published in the proceedings.

NUCLEAR REACTION ANALYSIS OF GLASS SURFACES: THE
STUDY OF THE REACTION BETWEEN WATER AND GLASS⁺

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ABSTRACT

Analysis for hydrogen and other light elements is notoriously difficult by most traditional analytic methods. Because of this, techniques based on nuclear reactions have been developed which can determine quantitatively the concentration profiles of hydrogen, oxygen and other elements. The use of the ¹⁵N hydrogen profiling, resonant oxygen scattering, and backscattering spectroscopy to study the changes in elemental composition near glass surfaces as a result of exposure to aqueous solution will be discussed as will the importance of these data to our understanding of the mechanisms of the reaction between water and glass. Combining these nuclear reaction techniques with electromigration or ion implantation to introduce "markers" makes it possible to study dissolution rates directly and to study the effects of ion implantation on both the ionic exchange and dissolution rate of glasses exposed to water

⁺Research supported by grants from the Office of Naval Research at Albany and from the NSF at RPI.

⁺⁺An Alfred P. Sloan Foundation Fellow.

Presented at International Conference on Ion Beam Modification of Materials, Grenoble, France, September 6-10, 1982, to be published in Nuclear Instruments and Methods.

Effects of Ion Implantation on the Reaction
Between Water and Glass +

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Abstract

The effect of ion implantation on the reaction between water and two glasses (fused silica, a commercial soda-lime glass) is investigated. Implantation of noble gas ions is seen to increase dramatically the rate of penetration of water into SiO_2 . The rate of penetration of water (hydrogen) into soda-lime glass is seen to increase and then decrease with implantation dose. Etch rates at 90°C in water and saline for implanted and unimplanted glasses are reported.

⁺ Research supported in part by a grant from the Office of Naval Research.

⁺⁺ An Alfred P. Sloan Foundation Fellow.